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PYROGENICS, INC.

# A Study of the Use of Vapor and Vacuum Deposition Technique For The Development Of High Strength Filamentary Materials

Quarterly Progress Report No. 1
Period: April 22, 1964 through July 22, 1964
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Reported by: J. R. Bedell
J. R. Bedell

Approved by: W. A. Robba
W. A. Robba

## Introduction:

Considerable research effort has been expended in recent years on the development of refractory high strength filamentary materials. Such materials when produced by evaporative or vapor conversion methods, have shown great promise, but have either not been dimensionally continuous, or have been limited in their strengths by the natures of the continuous substrates upon which they have been deposited.

Extremely high strength graphite whiskers of limited length have been generated via sublimation from a carbon arc by R. Bacon[1], and gas reaction graphite whiskers of similar geometric limitations and lower strengths have been produced by Meyer[2] and by Papaleges and Bourdeau[3]. Gas reaction coatings of pyrolytic graphite have been deposited on graphite yarns by Higgs[4] et al, Papalegis[3] and others, but the irregularities of the substrate surfaces have limited the product strength. Strong, extremely flexible sheet filaments of pyrolytic graphite have been produced by Robba[5], but these have yet to be generated in continuous form in thicknesses which will optimize strength.

Silicon carbide whiskers, produced by gas conversion, have possessed high strength, but have been non-uniform in physical properties and of limited lengths[6].

This contract was initiated with a thorough survey of literature pertaining to synthesis, treatment and properties of pyrolytic materials.

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A reference survey is presented in this report, indicating types of information available from various sources and designating, where possible, the pages upon which such information can be found.

Surveillance of this literature has indicated that the strengths of whiskers coatings and massive pyrolytic graphite deposits have been strongly influenced by three parameters:

1. Substratum Surface.
2. Specimen Thickness
3. Subsequent Treatment (i.e. annealing, hot and cold work)

Smooth substratums, thin deposits, and good orientation through treatment should provide an optimum pyrolytic filament. This program will consider these three parameters in the development of high strength filaments.

Author

Approach:

The surface upon which pyrolytic graphite shall be deposited will receive first attention in the course of this study.

Control of thickness and manner of deposition shall subsequently be considered. Improvement of properties by annealing and working shall then be attempted.

The substratum for pyrolytic deposition which will receive first consideration shall be a liquid surface. The deposition of a sheet filament upon a liquid surface suggests several useful applications to the production of strong continuous filament:

1. The surface should shear readily to permit continuous withdrawal of graphite film as it is generated over the liquid.

2. This ease of shearing may also permit fairly thin pyrolytic films to be generated and withdrawn without danger of rupture.

3. A liquid surface should maintain itself relatively free of imperfections and contribute strongly to the integrity and strength of film deposits.

4. By virtue of its perfection, a liquid surface should tend to be non-nucleating, and may thus permit an uninterrupted, continuous growth of graphite, initiated from a pyrolytic graphite seed.

5. A film grown on such a surface should be relatively free of those stresses often introduced by an unyielding, solid substratum.

A material which may serve as a liquid substratum for pyrolytic deposition of graphite must fulfill several requirements: It should be molten at graphite deposition temperatures; it must be incapable of forming carbides; it should have low solubility for carbon; its vapor pressure at graphite deposition temperatures should be negligible. Platinum possesses these properties, and experimental equipment is now being assembled to test the feasibility of pyrolysis on molten platinum. Should this approach be feasible, deposit properties as affected by deposition parameters shall be studied, and modifications shall be introduced to develop continuous filament approaches.

One alternate approach to substratum studies, which may be pursued if deposition on liquid metal is not feasible, will be the improvement of surface finish of graphite yarn prior to pyrolytic deposition.

Pyrolytic graphite coatings on batches of graphite yarn have been generated by Papalegis and Bourdeau[3], continuous coatings on graphite yarn by Higgs, et al[4], and continuous coatings on tungsten wire by Hough[7], in fulfillment of contracts for Wright-Patterson Air Force Base, but the effects of substrate modification have not been determined.

This approach will undertake to dissolve trace quantities of graphite from fiber surfaces by attack with boiling mercury, tin or zinc[(8)] to reduce irregularities on the substrate, and permit a controlled comparison of deposit strengths.

Other substratums which will be considered are polished rhenium and tantalum. Rhenium does not carburize, and, with its high temperature capability, may provide a very satisfactory surface for film deposition. Tantalum, which forms a tight, thin carbide film, also has promise as a deposition surface. A small quantity of rhenium foil has been ordered, and the tantalum is on hand.

Nickel foil has also been ordered in preparation for another approach to this program. At temperatures below the melting point of nickel (1453°C), carbon shall be pyrolytically deposited upon the nickel surface and subsequently the substratum shall be selectively etched away or evaporated. Attempts shall then be made to graphitize the pyrolytic carbon residue.

Continuous generation of graphite whisker by the stressing of filament above 3000°C shall be attempted. Carbon is to be supplied by sublimation from a hot graphite ring susceptor to the nucleation site from which the whisker is drawn. It is intended that stress and rapid diffusion of carbon along the whisker "a" planes to the nucleation site shall effect the continuous growth of whisker.

Following the determination of appropriate deposition surfaces, the limits of deposition thickness and their effects upon strength and integrity shall be explored.

The filamentary materials will then be subjected to annealing and working for improvement of properties. It is anticipated that thin deposits, being less prone to self-restriction of ordering, will permit better reorientation of structure by treatment.

| Reference No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Comment | Yes | Yes | Yes | Yes |
| Material | Graph. Whisks. | P. G. Whisks. | P. G. Whisks. | P. G. Filamnts. |
| Synthesis Pg. | 46, 197 | 451, 452 | 6, 8, 12, 13, 14, 15, 35 | 43-61 |
| Treatment | | | 15, 16 | |
| Thermal Conductivity | | | | |
| Electrical Conductivity | | | | |
| Thermal Expansion | | | | |
| Strength | | | 17, 18 | 47-55 |
| Elastic Modulus | 201 | | | |
| Hardness | | | | |
| Ductility | | | 18 | |
| Stress, Rupture, Creep | | | | |
| Density | | | | |
| Lattice, Structure, X-Ray | 47, 48, 49 197, 200 | 415, 452 453, 454 | 9, 18 | |
| Dislocations | | | | |
| Oxidation Resistance | | | 18, 19, 33 | |
| Metallography | | 454, 455 | | |
| Chemical Analysis | | | | |
| Other | | | | |

| Reference No. | 4 | 4 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| Comment | Yes | Yes | | Yes | Yes |
| Material | Massive P. G. | Vap. Dep. P. G. | SiC Whisk. | P. G. Filmnts. | |
| Synthesis | Pg.2-25 | 62-73 | 8-11, 26-31 | | |
| Treatment | 25-42 | | | | |
| Thermal Conductivity | | | | | |
| Electrical Conductivity | 34 | | | | |
| Thermal Expansion | 36 | | | | |
| Strength | 35 | | 32 | | |
| Elastic Modulus | 42 | | | | |
| Hardness | | | | | |
| Ductility | 37, 38, 39 | | | | |
| Stress, Rupture, Creep | | | | | |
| Density | 12, 13, 14, 32 | | | | |
| Lattice, Structure, X-Ray | | | | | |
| Dislocations | | | | | |
| Oxidation Resistance | | | | | |
| Metallography | | | | | |
| Chemical Analysis | | | | | |
| Other | | | | | |

| Reference No. | 9 | 10 | 10 | 11 | 11 | 11 |
|---|---|---|---|---|---|---|
| Comment | | | | | Yes | |
| Material | P. G. | P. G. | Pyro B. N. | Boron P. G. | P. G. | Pyro BN |
| Synthesis | Pg. | | | | | |
| Treatment | | | | | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | X | | | | 43, 44 | |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | 7 | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | |
| Lattice, Structure, X-Ray | 16 | | 135 | | | 44 |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | | | | |
| Chemical Analysis | | | | 43 | | |
| Other | | Electronic Properties | | | | |

| Reference No. | 12 | 12 | 13 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|
| Comment | | Yes | | | Yes | Yes |
| Material | Pyro BN | PG | PG | Glassy C | PG | PG |
| Synthesis Pg. | | | | 46 | | |
| Treatment | | | | | 41, 42 | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | 54 | | 46 | 42 | 20 |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | 52-54 | | 46 | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | |
| Lattice, Structure, X-Ray | 50 | 54 | 45 | | 42, 43 | 23 |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | | | | 22 |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|
| Comment | | Yes | Yes | Yes | Yes | |
| Material | | PG | PG | PG | PG | Boron PG |
| Synthesis | Pg. | | | | | 71 |
| Treatment | | 19 | 18, 19 | 86, 87, 88 | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | 15, 16 | | 87, 90 | 78 | 72 |
| Elastic Modulus | | | | 88 | | |
| Hardness | | | | | | |
| Ductility | | 15, 16 | | 79, 87, 88, 90 | 79 | 72 |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | 71 |
| Lattice, Structure, X-Ray | | 19, 20 | 18, 19, 20 | 88, 89 | | |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | | 87, 89 | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 21 | 22 | 23 | 23 | 24 |
|---|---|---|---|---|---|
| Comment | | Yes | | | Yes |
| Material | PG | PG | Boron PG | PG | PG |
| Synthesis Pg. | | | | | 2 |
| Treatment | 119 | 100 | | | |
| Thermal Conductivity | | | | | |
| Electrical Conductivity | | | | | |
| Thermal Expansion | | | | | |
| Strength | | | 3,4 | 4 | |
| Elastic Modulus | 120 | | | | |
| Hardness | | | | | |
| Ductility | | 100 | 3,4 | 4 | |
| Stress, Rupture, Creep | | | | | |
| Density | | | | | 2 |
| Lattice, Structure, X-Ray | 118, 119 | | 5,6,7 | | 2-8,9 |
| Dislocations | | | | | |
| Oxidation Resistance | | | | | |
| Metallography | | | | | 2 |
| Chemical Analysis | | | 2,8 | | |
| Other | | | | | |

| Reference No. | 25 | 26 | 27 | 28 | 29 | 29 |
|---|---|---|---|---|---|---|
| Comment | Yes | (Ref. to hi film strngth) | Yes | Yes | Yes | Yes |
| Material | Graph. | PG | PG | PG | PG | PG Whsks. |
| Synthesis Pg. | | 1,3,4 | | 468 | 816,817,820 | 820 |
| Treatment | | | | 468 | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | 469 | | |
| Thermal Expansion | | | | | | |
| Strength | 493,495 | 5 | 485 | | | |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | |
| Lattice, Structure, X-Ray | | 2,3 | | | 816,817 | |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | 490 | 4 | | | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | | 30 | 31 | 32 | 33 | 34 |
|---|---|---|---|---|---|---|
| Comment | | Yes | Yes | Yes | Yes | Yes |
| Material | | PG | PG | PG | Graph. | $Al_2O_3$ |
| Synthesis | Pg. | 105, 108 | | 1066 | | |
| Treatment | | 107, 108 | | 1066 | | |
| Thermal Conductivity | | 107 | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | 107 | | | | |
| Strength | | 106, 107 | x | | | 67, 69, 71 |
| Elastic Modulus | | | | 1066, 1067 | | |
| Hardness | | 106 | | | | |
| Ductility | | | x | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | 104 | | 1066 | | |
| Lattice, Structure, X-Ray | | 105, 107, 108 | x | | | |
| Dislocations | | | | | x | |
| Oxidation Resistance | | 105, 106 | | | | |
| Metallography | | | | | | |
| Chemical Analysis | | | | | | |
| Other | | Specific ht. | | | | |

| Reference No. | 34 | 35 | 36 | 37 | 38 | 39 |
|---|---|---|---|---|---|---|
| Comment | | Yes | Yes | Yes | Yes | |
| Material | ATJ Graph., PG | | | | $Al_2O_3$ | $Al_2O_3$ Whiskers |
| Synthesis Pg. | | | | | | 34,35 |
| Treatment | | | | | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | 61-6,69,70, 72,73,74 | | | | 299 | 35,36,38 |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | 37 |
| Density | | | | | | |
| Lattice, Structure, X-Ray | | | | | | |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | | | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 40 | 41 | 42 | 43 | 44 | 45 |
|---|---|---|---|---|---|---|
| Comment | Yes | Yes | Yes | Yes | Yes | |
| Material | | | | | PG & other mtrl. | PG |
| Synthesis Pg. | | | | | x | 168, 169 |
| Treatment | | | | | | |
| Thermal Conductivity | | | | | 7 | 168, 169 |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | | | | 13 | |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | x | |
| Lattice, Structure, X-Ray | | | | | | |
| Dislocations | | | | | | 168-170 |
| Oxidation Resistance | | | | | | |
| Metallography | | | | | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 46 | 47 | 48 | 49 | 50 | 51 |
|---|---|---|---|---|---|---|
| Comment | Yes | Yes | Yes | Yes | | Yes |
| Material | PG | PG | Superalloys & T.D. Ni | Graphite | Graphite Yarns | Grpht. |
| Synthesis | Pg. | | | x | | |
| Treatment | | | | | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | | x | | 592-594 | |
| Elastic Modulus | | 3 | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | 2, 9 | | | | |
| Lattice, Structure, X-Ray | | 13 | | x | | |
| Dislocations | | | | | | x |
| Oxidation Resistance | | | | | 590, 591 | |
| Metallography | | | | | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 52 | 53 | 54 | 55 | 56 | 57 |
|---|---|---|---|---|---|---|
| Comment | | | | | Yes | Yes |
| Material | C Whisks. | Graphite Whisks. | PG | PG | PG Graphite | PG |
| Synthesis Pg. | 309 | 29,30 | | | | |
| Treatment | | | | 85 | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | | | | | |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | |
| Lattice, Structure, X-Ray | | | 467 | 83, 84, 85 | | |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | 469, 470 | 83, 84, 85 | 109-111 | 114, 116, 118 |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 58 | 59 | 60 | 61 | 62 | 63 |
|---|---|---|---|---|---|---|
| Comment | | | | Yes | Yes | Yes |
| Material | Grpht. | Grpht. | PG | C, Grpht. | PG | Grpht. PG |
| Synthesis | Pg. | X | | | | |
| Treatment | | | X | 772 | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | |
| Strength | | | | | | |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | 57 |
| Lattice, Structure, X-Ray | | | x | 772 | | 57,58,59 78,79 |
| Dislocations | — | | | | | |
| Oxidation Resistance | x | | | | | |
| Metallography | x | | | | 3386 | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 64 | 65 | 66 | 67 |
|---|---|---|---|---|
| Comment | | Yes | Yes | Yes |
| Material | $H_2C$, $CH_4$ | Graphite | Graphite | Graphite Whiskers |
| Synthesis Pg. | X | | 10 | 90, 174, 175 |
| Treatment | | | | |
| Thermal Conductivity | | | | |
| Electrical Conductivity | | | | |
| Thermal Expansion | | | | |
| Strength | | 102, 103 | | 90, 91, 97, 98 99, 103, 180-183 |
| Elastic Modulus | | | | |
| Hardness | | | | |
| Ductility | | | | |
| Stress, Rupture, Creep | | | | |
| Density | | | | |
| Lattice, Structure, X-Ray | | | 10 | 100-103 |
| Dislocations | | | | 103 |
| Oxidation Resistance | | | | |
| Metallography | | | | |
| Chemical Analysis | X | | | |
| Other | | | | |

| | | |
|---|---|---|
| Reference No. | 68 | 68 |
| Comment | Yes | |
| Material | Graphite | PG |
| Synthesis . Pg. | | |
| Treatment | | |
| Thermal Conductivity | | |
| Electrical Conductivity | | |
| Thermal Expansion | | |
| Strength | 19,20,21 | 22 |
| Elastic Modulus | | |
| Hardness | | |
| Ductility | | |
| Stress, Rupture, Creep | | |
| Density | | |
| Lattice, Structure, X-Ray | | |
| Dislocations | | |
| Oxidation Resistance | | |
| Metallography | | |
| Chemical Analysis | | |
| Other | | |

| Reference No. | 69 | 69 | 70 | 71 | 72 | 73 |
|---|---|---|---|---|---|---|
| Comment | Yes | | Yes | Yes | Yes | Yes |
| Material | PG | Boron PG | PG | PG | Grpht. Whskr. | SiC, WC, TaC, NbC, HfC, ZrC, TiC |
| Synthesis | Pg. 61 | | | | | |
| Treatment | 62 | 63, 64 | | 1193 | | |
| Thermal Conductivity | 61, 64, 67 | | | 1192, 1193 | | X |
| Electrical Conductivity | 62, 63 | 63 | X | 1192, 1193 | | |
| Thermal Expansion | 62 | | | | | |
| Strength | | | | | | |
| Elastic Modulus | | | | | | X |
| Hardness | | | | | | |
| Ductility | | | | | | |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | |
| Lattice, Structure, X-Ray | 60, 62 | | | 1193 | | X |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | | | | 111 |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 74 | 75 | 76 | 77 | 78 | 79 |
|---|---|---|---|---|---|---|
| Comment | | Yes | | Yes | Yes | |
| Material | PG | C | $TiB_2$ | | SiC | Petroleum Coke Graph. |
| Synthesis | Pg. | | | | X | |
| Treatment | | | | | | |
| Thermal Conductivity | | | | | | |
| Electrical Conductivity | | | | | | |
| Thermal Expansion | | | | | | 7, 8 |
| Strength | | | | | | 8, 9 |
| Elastic Modulus | | | | | | |
| Hardness | | | | | | |
| Ductility | | | | | | 8 |
| Stress, Rupture, Creep | | | | | | |
| Density | | | | | | 3 |
| Lattice, Structure, X-Ray | | | | | | |
| Dislocations | | | | | | |
| Oxidation Resistance | | | | | | |
| Metallography | | | X | | | |
| Chemical Analysis | | | | | | |
| Other | | | | | | |

| Reference No. | 80 | 81 | 82 | 83 | 84 | 85 | 86 |
|---|---|---|---|---|---|---|---|
| Comment | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Material | Bromine PG | PG | PG | PG | PG | PG | PG |
| Synthesis | Pg. X | 171-174, 177, 178 | | | 21 | 2 | |
| Treatment | | | 52, 56, 54 | X | 26 | | |
| Thermal Conductivity | | | 1, 8 | | | | |
| Electrical Conductivity | | | 8, 56 | | 25 | | |
| Thermal Expansion | X | | 8, 54 | 6, 7, 15 | | 5 | |
| Strength | | 173, 174, 176 | 9, 10, 11, 52 | | | | |
| Elastic Modulus | | | 9, 11 | | | | |
| Hardness | | | | 4, 15, 17 | | | |
| Ductility | | | | | | | |
| Stress, Rupture, Creep | | | | | | | |
| Density | | | 8, 26 | 10 | | | |
| Lattice, Structure, X-Ray | | | 3 | 7, 13, 19 20, 21 | 24, 25, 26 | 2, 4, 5 | |
| Dislocations | | | | | | | |
| Oxidation Resistance | | | | | | | |
| Metallography | | | | 3 | | 3 | |
| Chemical Analysis | | | | | | | |
| Other | | | Emissivity, Specific Ht., | | | | |

| No. | Reference | Comment |
|---|---|---|
| 1. | R. Bacon, "The Structure and Properties of Graphite Crystals", from "Growth and Perfection of Crystals", John Wiley & Sons, N.Y., 1958 | Excellent treatise on graphite whisker growth and physical testing. |
| 2. | L. Meyer, "Graphite Whiskers", Proc. of the 3rd Conference on Carbon, Pergamon Press, Inc., 1959 | Discussion of growth mechanism and high diffusion rate along basal planes. |
| 3. | F.E. Papalegis and R.G. Bourdeau, "Pyrolytic Reinforcing Agents for Ablative Erosion-Resistant Composites", ASD-TDR-63-403, May, 1963. | Very informative summary. Whisker growth, batch filament coating. |
| 4. | Higgs, Finicle, Bobka, Seldin & Zeitsch, "Research and Development on Advanced Graphite Materials, Vol. XXXVII - Studies of Graphite Deposited by Pyrolytic Processes" WADD TR61-72, May 1964. | PG deposition on graphite yarn by resistance heating. Excellent investigation of numerous parameters and their effects upon synthesis and properties. PG by evaporation. |
| 5. | W.A. Robba, Pyrogenics personal communication, 1964 | |
| 6. | L.A. Yerkovitch and H.P. Kirchner, "Growth and Mechanical Properties of Filamentary Silicon Carbide Crystals", WADD TR61-252, June 1962 | |
| 7. | R.L. Hough, "Refractory Reinforcements for Ablative Plastics, Part IV: Synthesis Apparatus for Continuous Filamentous Reinforcements", ASD-TDR-62-260, Part IV, Dec. 1963. | Continuous PG filaments deposited over resistance heated tungsten wire. |
| 8. | M. Hansen, "Constitution of Binary Alloys", McGraw Hill, 1958, p. 348 | "Boiling mercury, cadmium, tin and zinc dissolve only traces or unweighable amounts of carbon which precipitate on cooling in the form of graphite". |

| No. | Reference | Comment |
|---|---|---|
| 9. | W.V. Kotlensky and H.E. Martens "Tensile Properties of Pyrolytic Graphite to 5000°F" Report No. 32-71, JPL, March 10, 1961. | |
| 10. | W.V. Kotlensky and D.B. Fischbach "Space Program Summary" Report No. 37-17, Vol. IV, JPL, Oct. 30, 1962 | |
| 11. | A.W. Thompson "Space Program Summary" Report No. 37-21, Vol. IV, JPL, June 30, 1963 | Flexure Testing of PG |
| 12. | D.B. Fischbach, W.V. Kotlensky and A.W. Thompson "Space Program Summary: Report No. 37-22, Vol. IV, JPL, Aug. 31, 1963 | Orientation vs. strength and ductility; 2-stage deformation. |
| 13. | D.B. Fishbach "Space Program Summary" Report No. 37-24, Vol. IV, JPL, Dec. 31, 1963 | |
| 14 | W.V. Kotlensky "Space Program Summary" Report No. 37-25, Vol. IV, JPL, Feb. 29, 1964 | Mechanical forming of PG. Activation energy studies for PG formation, p. 43, 44, 45 |
| 15. | "Research Summary" Report No. 36-4, Vol. II, JPL, Sept. 1, 1960. | Kinking effect by tensile test. Effects of heating and deformation on graphitization. |
| 16. | "Research Summary" Report No. 36-5 Vol. II., JPL, Nov. 1, 1960 | Growth Data |
| 17. | "Research Summary" Report No. 36-6, Vol. II., JPL, Jan. 2, 1961 | Discussion of structure of PG and crystalline Graphite. |
| 18. | "Research Summary" Report No. 36-8, Vol. IV, JPL, May 1, 1961 | Discussion (p. 90,91) of orientation, structure and deformation. |
| 19. | "Research Summary" Report No. 36-10, Vol. I, JPL, Aug. 1, 1961 | Effects of strain rate. Effects of growth cones upon strength. |
| 20. | "Research Summary" Report No. 36-11, JPL, Nov. 1, 1961 | |
| 21 | "Research Summary" Report No. 36-12, Vol. I, JPL, Jan. 2, 1962. | |

| No. | Reference | Comment |
|---|---|---|
| 22 | "Research Summary" Report No. 36-13 JPL, March 1, 1962 | "Elimination of growth cone structure" p 99 |
| 23 | W. V. Kotlensky and H.E. Martens, "Structural and High Temperature Tensile Properties of Boron Pyrolytic Graphite", Report No. 32-299, JPL, Dec. 16, 1963 | Good reference source for structural studies of PG |
| 24 | W. V. Kotlensky and H.E. Martens, "Structural Transformation in Pyrolytic Graphite Accompanying Deformation", Report No. 32-360, JPL, Nov. 1, 1962 | Good discussion of deformation mechanism. |
| 25 | R. J. Diefendorf, "The Effect of Atmosphere on the Strength of Graphite", Proceedings of the Fourth Conference on Carbon, 1960 | Utilization of bend test accommodating numerous specimens at temperature and in vacuo simultaneously. |
| 26 | T. J. Clarke, "Discussion with Dr. Diefendorf on mechanism of Graphite Formation, BNL, August 29, 1962 | High film strength at 50-150Å |
| 27 | R. J. Diefendorf "The Mechanical Strength of Pyrolytic Graphite", Proceedings of the Fourth Conference on Carbon, 1960 | Effects of gas contamination on loss of shear strength between basal planes. |
| 28 | C. A. Klein, W.D. Straub, and R. J. Diefendorf, "Evidence of Single-Crystal Characteristics in Highly Annealed Pyrolytic Graphite", Physical Review, Vol. 125, No. 2, Jan. 15, 1962 | Heat treatment at 3600°C produces essentially single crystal characteristics. |
| 29 | R. J. Diefendorf, "The Deposition of Pyrolytic Graphite", Journal de Chimie Physique 57, 1960 | PG growth on filaments, p. 816 Gas transformation and deposition mechanics, p 818 - 820. |
| 30 | R. J. Diefendorf and E. R. Stover, "Pyrolytic Graphite --- How Structure Affects Properties", Metal Progress May, 1962 | Good discussion of growth and of structural effects by annealing. |

| No. | Reference | Comment |
|---|---|---|
| 31. | H.E. Martins and W.V. Kotlensky, "Tensile Behavior of Pyrolytic Graphite at 2,750°C", Nature, Vol. 186, No. 4729, June 18, 1960 | Testing in helium. 3-dimensional ordering increased with deformation. |
| 32. | W.V. Kotlensky, K.H. Titus, Jr., and H.E. Martens, "Young's Modulus of Hot-Worked Pyrolytic Graphite", Nature, Vol. 193, No. 4820, March 17, 1962 | Suggests 16% deformation at 2,750°C has very real benefits. |
| 33. | A. Grinall and A. Sosin, "Dislocations in Graphite", Proceedings of the Fourth Conference on Carbon, 1960 | Discussion of slip mechanism. Good models of structure. |
| 34. | "The True Stress-Strain Properties of Brittle Materials to Very High Temperatures", Report No. 6387-1190-XXXV, Southern Research Institute, Sept. 13, 1963 | Thorough description of very high temperature tensile testing furnace. |
| 35. | J.R. Priest, "Apparatus for the Measurement of Stress in Vacuum Evaporated Films", The Review of Scientific Instruments, Vol. 32, No. 12, Dec. 1961 | Measurement of substrate deflection. |
| 36. | D. Kuhlmann-Wilsdorf and K. Srinivasa Raghavan, "New Tensile Testing Machine for Thin Specimens", The Review of Scientific Instruments, Vol. 33, No. 9 Sept., 1962. | Appears applicable for room and high temperature testing of films and wires. |
| 37. | F.D. Lemkey and R.W. Kraft, "Tensile Testing Technique for Submicron Specimens", The Review of Scientific Instruments, Vol. 33, No. 8, Aug., 1962. | Interesting for fiber testing, probably only room temperature |
| 38. | R. Sedlacek and F.A. Halden, "Method for Tensile Testing of Brittle Materials", The Review of Scientific Instruments, Vol. 33, No. 3, March, 1962. | For room temperature testing of hollow cylinders. |

| No. | Reference | Comment |
|---|---|---|
| 39. | S.S. Brenner, "Mechanical Behavior of Sapphire Whiskers at Elevated Temperatures", Journal of Applied Physics, Vol. 33, No.1, Jan., 1962. | |
| 40. | D. M. Marsh, "Micro-Tensile Testing Machine", Journal of Scientific Instruments, Vol. 38, June, 1961. | Machine, apparently manufactured, for testing whiskers and fibers. |
| 41. | H.B.M. Wolters and F.W. Schapink, "Tensile Testing Machine for Whiskers", Journal of Scientific Instruments, Vol. 38, June, 1961. | Whiskers bonded to machine by S-diphenyl carbazide adhesive. |
| 42. | A.E. Widdowson, "A Simple Tensile Testing Machine for Very Fine Wires", Journal of Scientific Instruments, Vol. 35, March, 1958. | Wire $\sim$ 1 ft. long; spring deflection indicates load; vernier indicates deflection. |
| 43. | J. L. Taylor, "Apparatus for Tensile Testing to 5400°F in Vacuo", Review of Scientific Instruments, Vol. 34, No. 5, May, 1963. | Induction heated tensile equipment; heated tungsten grips; moly alloy ball joints |
| 44. | "Cambridge Conference on Strength of Metal Whiskers and Thin Films", ORNL-34-58 April 17, 1958. | Good discussion of whisker and film theory. |
| 45. | D.B. Fischbach, "Kinetics of High-Temperature Structural Transformation in Pyrolytic Carbons", Applied Physics Letters, Vol. 3, No. 9, Nov. 1, 1963. | |
| 46. | J. Harvey, D. Clark and J. N. Eastabrook, "The Structure of Pyrolytic Carbon", UDC No. 661-666, Royal Aircraft Establishment, Oct., 1962. | Cone formation and causes. |
| 47. | L. Marcus, "Modulus of Rupture Tests on Pyrolytic Graphite", BLR 62-13(M), Revision A, Oct. 31, 1962 | Bending Tests and mathematical stress studies. |

| No. | Reference | Comment |
|---|---|---|
| 48. | "Ultra-Fine High-Temperature, High Strength Metallic Fibers", ASD-TDR-62-727, Part 1, Aug., 1962. | Superalloy wires, drawn ~ .001". Slitting, winding, sheathing, testing. |
| 49. | B.E. Warren, "X-Ray-Study of the Graphitization of Carbon Black", Proceeds of the First and Second Conferences on Carbon, Waverly Press, 1962. | Discussion of orientation and alignment by heat treatment. |
| 50. | G.E. Cranch, "Unique Properties of Flexible Carbon Fibers", Proceeds of the Fifth Conference on Carbon, Macmillan Press, 1963. | |
| 51. | T. Tsuzuku, "Dislocations in Graphite Crystals", Proceeds of The Third Conference on Carbon. | Growth and slip of graphite crystals. |
| 52. | C.R. Kinney and R.S. Slysh, "Carbonization of Benzene, Acetylene and Diacetylene at 1200°C", Proceeds of the Fourth Conference on Carbon, Pergamon Press, 1960. | |
| 53. | K.W. Sykes, "The Preparation and Study of Evaporated Carbon Films", Proceeds of The Fourth Conference on Carbon, 1960. | |
| 54. | G. Susich and L.M. Dogliotti, "The Microscopic Structure of Pyrographite", Proceeds of the Fifth Conference on Carbon. | |
| 55. | W.C. Coons "A Rapid Method for Polishing Pyrolytic Graphite" Metal Progress, June 1962. | |
| 56. | T.V. Brassard and A.S. Holik, "Preparing Various Graphites for Metallographic Examination", Metal Progress, May, 1962. | Sensitive tint vs. straight polarized illumination; vibratory and rotary polishing, etc. |
| 57. | W.C. Coons, "More on Polishing Pyrolytic Graphite" Letter to Editor, Metal Progress, May, 1963. | Comparison of polishing methods. |
| 58. | E.E. Glenda Hughes, B.R. Williams and J.M. Thomas, "Etching of Graphite Surfaces with Oxygen", Transactions of The Faraday Society, Vol. 58, No. 478, Oct. 1962 | |

| No. | Reference | Comment |
|---|---|---|
| 59. | P.W. Levy, "Suggested Method for the Growing of Graphite Crystals", BNL, Sept. 14, 1955 | |
| 60. | O.J. Guentert, "X-Ray Study of Pyrolytic Graphites", Journal of Chem. Physics, Vol. 37, No. 4, Aug. 15, 1962 | |
| 61. | T. Noda, M. Inagaki, "Heat Treatment of Carbon Under Various Pressures", Nature, Vol. 196, Nov. 24, 1962. | More rapid graphitization in air than in vacuo. |
| 62. | A. Tarpinian, "Recrystallized Microstructures of Pyrolytic Graphite", Applied Physics, Vol. 33, No. 11, Nov. 1962. | Electron microscopy of peeled pyrolytic graphite layers. |
| 63. | C.A. Klein, "Electrical Properties of Pyrolytic Graphites", Reviews of Modern Physics, Vol. 34, No. 1, Jan., 1962 | Formula definition for degree of graphitization, p. 59. |
| 64. | K. Hedden, "The Formation of Methane from Hydrogen and Carbon at High Temperatures and Pressures", Proceeds of the Fifth Conference on Carbon, Macmillan Press, 1963. | |
| 65. | G.W. Rowe, "High Temperature Strength of Clean Graphite", Nuclear Engineering, March 1962. | Effects of gas contamination, vacuum and heat upon graphite strength. |
| 66. | T. Noda, M. Inagaki, "Effect of Atmosphere on Graphitization of Carbon", Sixth Biennial Conference on Carbon, 1963. | $O_2$ and $CO_2$ accellerate graphitization. |
| 67. | "Research and Development on Advanced Graphite Materials, Summary Technical Report", WADD TR61-72, Vol. XLII, Aug., 1963. | Graphite cement formulation. Large diameters reduce whisker strength. Whiskers by 3 methods, 2 at one atm. Low temp. whiskers weaker. Very comprehensive. |

| No. | Reference | Comment |
|---|---|---|
| 68. | M.B. Manofsky and R.B. Dull, "Research and Development on advanced Graphite Materials, Methods of Measuring Mechanical Properties of Graphite in the 20° to 2700°C Temperature Range", WADD TR 61-72, Vol. XXXV, April, 1964. | Excellent study of graphite tensile, compressive, flexural and shear strength study, and equipment development. |
| 69. | C.A. Klein, "Pyrolytic Graphite", International Science and Technology, Aug. 1962. | Applications of PG and properties. |
| 70. | A.R. Ubbelohde, "British Progress in Pyrolytic Graphite", Letter to Editor, Source unknown. | Electrical anisotropy and uses for thermoelectric devices. |
| 71. | A.R. Ubbelohde, D.A. Young and A.W. Moore, "Annealing of Pyrolytic Graphite Under Pressure", Nature, Vol. 198, No. 4886, June 22, 1963. | Recommends 3,500°C for satisfactory ordering. |
| 72. | F.R. Rollins, Jr. "Use of Graphite Whiskers in a Study of the Atmosphere Dependence of Graphite Friction", Journal of Applied Physics, Vol. 32, No. 8, Aug. 1961. | Technique of bonding whiskers to mounts. Study of wear and friction. |
| 73. | Pyrofiber Free-Standing Pyrographite and Pyrocarbide" Task III, AD298720, Jan. 1963. | Apparatus, controls, phase diagrams. Hi strength with 25 wt% ZrC. |
| 74. | A.R.G. Brown and W. Watts "The Preparation and Properties of High-Temperature Pyrolytic Carbon", Industrial Carbon and Graphite Conference, Society of Chemical Industry, London, 1958. | |
| 75. | T.D. Davidson, "Application of Sonic, Ultrasonic and Inductive Techniques to the Non-Destructive Testing of Carbon", Industrial Carbon and Graphite Conference, London, 1958. | Young's modulus, shear modulus, Poisson's ratio by sonic resonance and U/S pulse velocity, and detection of variations such as cracks, hardness, density, etc. |

| No. | Reference | Comment |
| --- | --- | --- |
| 76. | C.T. Lynch, F.W. Vahldiek, S.A. Mersol and C.R. Underwood, "Investigation of Single-Crystal and Polycrystalline Titanium Diboride: Metallographic Procedures and Findings" ASD TR61-350, Nov., 1961. | |
| 77. | J.E. Emrick and H.L. Gegel, "A Tensile Testing Apparatus for Short Fine Filaments with Optical-Mechanical Strain Measurement", ASD TR 61-168, Sept. 1961. | Indication of good reproducibility with calibrated springs. |
| 78. | J. M. Blocher, D.P. Leiter and R.P. Jones, "Coating of Graphite with Silicon Carbide by Reaction with Vapor of Controlled Silicon Activity", BMI-1349, June 15, 1959. | Coatings formed by decomposition of $SiI_4$ and reaction with carbon base. |
| 79. | H.E. Martens and W.V. Kotlensky "Structural and High Temperature Tensile Properties of Special Pitch-Coke Graphites", Technical Report No. 32-181, JPL, Nov. 30, 1961. | |
| 80. | W. H. Martin and J.E. Brocklehurst, "The Thermal Expansion Behaviour of Pyrolytic Graphite-Bromine Residue", Carbon, Vol. 1, No. 2, Feb. 1964. | High expansion via exfoliation from interlayered bromine. |
| 81. | R.H. Bragg, D.D. Crooks, R.W.Fenn, Jr. and M.L. Hammond, "The Effect of Applied Stress on the Graphitization of Pyrolytic Graphite", Carbon, Vol. 1, No. 2, Feb. 1964. | Discussion of mechanics of graphitization. |
| 82. | W.D. Bradshaw and J.R. Armstrong, "Pyrolytic Graphite, Its High Temperature Properties", ASD-TDR-63-195, March 1963. | Anisotropy effects, treatment. Very informative PG fabrication reference. |

| No. | Reference | Comment |
|---|---|---|
| 83. | E. R. Stover, "Effects of Annealing on the Structure of Pyrolytic Graphite", 60-RL-2564M, TID-12542, Nov., 1960. | Discussion of annealing mechanism and effects thereof. |
| 84. | L. C. F. Blackman and A. R. Ubbelohde, "Stress Recrystallization of Graphite", Proceeds of Royal Society A, Vol. 266. | Residual stresses in PG. Measurement of mean interlayer spacings. Structure according to thickness. One-second stress transformation and explosive transformation. |
| 85. | J. H. Richardson and E. H. Zehms, "Materials and Structures - Physical Measurements Program", Oct. 1, 1962. | Singularly vs. continuously nucleated PG. |
| 86. | D. B. Murphy, H. B. Palmer and C. R. Kinney, "A Kinetic Study of the Deposition of Pyrolytic Carbon Films", Industrial Carbon and Graphite, Society of Chemical Industry, 1958. | |